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(64) **Glass composition and use.**

(57) A glass composition capable of being spun into fibres has the following components expressed as weight percent :  $\text{SiO}_2$  - 66 to 73 ;  $\text{Al}_2\text{O}_3$  - 0.85 to 5 ;  $\text{R}_2\text{O}$  (=  $\text{Na}_2\text{O}$  +  $\text{K}_2\text{O}$ ) - 14 to 17.5 ;  $\text{CaO}$  - 6.5 to 12 ; and  $\text{SiO}_2$  +  $\text{Al}_2\text{O}_3$  - 69 to 74. The composition is free of boric oxide and consequently avoids pollution difficulties associated with that compound, yet it can be used in high temperature spinners to produce durable fibres.

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This invention relates to a boric oxide free glass composition capable of being spun into fibres, it also relates to a method of spinning compositions according to the invention in a spinner made from a mechanically alloyed or oxide dispersion strengthened alloy and to glass fibre insulation produced from the compositions according to the invention.

6 Glass compositions are known for use in the technique of fiberizing glass using a centrifugal spinner. The compositions have customarily incorporated boric oxide in order to give them temperature/viscosity characteristics that will enable the glass to pass freely through orifices in the centrifugal spinner wall at a temperature sufficiently low to prevent excessive corrosion and erosion of the spinner. A problem with the use of boric oxide is that boron is volatile and may escape from the glass melting tank to cause pollution problems. Furthermore  
10 it tends to condense on regenerators thereby fouling them up and preventing use of such devices to improve the thermal efficiency of fuel fired glass melting tanks.

GB 2 041 910 proposes the reduction or elimination of boric oxide with a consequent rise in liquidus temperature and high levels of alumina or baria. These reduced boric oxide compositions are acknowledged to be virtually impossible to fiberize on an industrial basis by the prior art spinning techniques. A technique involving  
15 the use of a novel spinner shape is proposed, but, in practice, the corrosion of such a spinner when fabricated from conventional alloy is unacceptably high. Also the glass compositions according to this patent have unacceptably low durability.

US Patent 4 402 767 proposes a novel spinner fabrication process to produce a mechanically alloyed or oxide dispersion strengthened alloy by a combination of warm working, annealing and hot forming processes.  
20 Such spinners are claimed to have excellent resistance against molten glass attack and are said to be capable of producing glass fibres and mineral wool at temperatures as high as 1315°C. No details of glass fibre production are given in the specification.

The problem has been to identify boron free glass compositions which have the required durability and can be used in high temperature spinners such as those described in US 4 402 767. Although the absence of boric  
25 oxide gives rise to a deterioration in the aqueous durability of the glass, we have identified a range of compositions for which the durability is satisfactory.

According to the present invention a boric oxide free glass composition capable of being spun into fibres, comprises the following components, expressed as weight percent:

SiO <sub>2</sub>	66-73
Al <sub>2</sub> O <sub>3</sub>	0.8-5
R <sub>2</sub> O = Na <sub>2</sub> O + K <sub>2</sub> O	14-17.5
CaO	6.5-12
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	69-74

Such glasses have a viscosity of 1000 poise or less at temperatures up to about 1200°C and a liquidus at least  
35 130°C below the 1000 poise temperature.

The composition may also contain : 0-2% Fe<sub>2</sub>O<sub>3</sub>; 0-5% MgO; 0-0.6% SO<sub>3</sub>, all expressed as weight percent.

Preferably the components are present in weight percentages within the following ranges:

SiO <sub>2</sub>	67-72.4
Al <sub>2</sub> O <sub>3</sub>	1-4
40 R <sub>2</sub> O	14.5-17
K <sub>2</sub> O	0.5-2
Na <sub>2</sub> O	13.5-16.5
CaO	7-11.2
Fe <sub>2</sub> O <sub>3</sub>	0.1-2.5
45 MgO	0.2-4.4
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	70-73.7

Most preferably the components are present in weight percentages within the following ranges

SiO <sub>2</sub>	67-70
Al <sub>2</sub> O <sub>3</sub>	2-4
50 Na <sub>2</sub> O	14-15.5
K <sub>2</sub> O	0.5-1.5
MgO	3-4.5
CaO	7-8.5
Fe <sub>2</sub> O <sub>3</sub>	0.3-2
55 SO <sub>3</sub>	0-0.3
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	70-72
Na <sub>2</sub> O + K <sub>2</sub> O	15-16.5

A high level of Na<sub>2</sub>O is needed to give a low liquidus temperature but the preferred narrow range of MgO

allows the  $\text{Na}_2\text{O}$  to be kept to a minimum so optimising durability while maintaining liquidus at least 160 centigrade degrees below the 1000 poise viscosity temperature, which is advantageously below 1170°C.

The invention will now be described with reference to the following non-limiting examples 1-28. Low levels of  $\text{SO}_3$ ,  $\text{K}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  are recorded as a minimum in these examples. In fact they are only present at the lower levels as impurities in the raw materials and do not make a significant contribution to the properties of the glass fibres. Details of the examples and durability tests are given in the Table. It should be noted that Example 18 falls outside the scope of the present invention as its low level of alumina renders it insufficiently durable.

There is no established international test procedure for assessing the suitability of a glass for glass fibre insulation applications. It has become the practice to use the laboratory ware test of ISO 719 as it gives a useful guide to the aqueous durability and weathering resistance of the glass. In this test 2g of glass grains are treated with distilled water for 60 mins at 98°C and the extracted alkali titrated against 0.01 M HCL. The durability is described in terms of the alkali extracted per gram of glass as calculated from the acid required to neutralise. The relevant classes for glass wool are ISO Class 3 - from 62 to 264 micrograms of alkali per gram; and Class 4 - from 265 to 620 micrograms per gram. Glass wool is preferably in Class 3 but a good Class 4 may be acceptable because the performance of the insulation is a function of both glass and resin binder, and binders are available for use with higher release glasses. A class 3 rating is good and a class 4 rating is acceptable, but not as good.

Table 1

Example	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	70	69	68	67	70	69	67	67
Al <sub>2</sub> O <sub>3</sub>	1	2	3	4	3	3	3	3
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	71	71	71	71	73	72	70	70
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
CaO	8	8	8	8	8	8	8	9
MgO	4	4	4	4	4	4	4	4
Na <sub>2</sub> O	15.5	15.5	15.5	15.5	13.5	14.5	16.5	15.5
K <sub>2</sub> O	1	1	1	1	1	1	1	1
R <sub>2</sub> O	16.5	16.5	16.5	16.5	14.5	15.5	17.5	16.5
SO <sub>3</sub>	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tlog <sub>3</sub>	1146	1150	1155	1159	1191	1173	1136	1142
Liquidus	952	964	982	1002	1012	1002	980	1018
μgR <sub>2</sub> O/g	307	270	260	248	186	251	406	285
Class	4	4	3	3	3	3	4	4

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Example	9		10			11		12		13		14		15		16	
S102	69		68.5			69		68		72.4		70		68		68	
A1203	3		3			3		3		1.3		3		4		3	
S102+A1203	72		71.5			72		71		73.7		73		72		71	
Fe2O3	0.3		0.3			0.3		1.3		0.1		0.3		0.3		1.9	
CaO	7		8			7.5		7.5		11.2		8.3		7.5		8	
MgO	4		4			4		4		0.2		3.9		3.5		3.9	
N2O	15.5		15			15		15		14		13.5		15.5		14	
K2O	1		1			1		1		0.5		0.9		1		1	
R2O	16.5		16			16		16		14.5		14.4		16.5		15	
SO3	0.2		0.2			0.2		0.2		0.2		0.2		0.2		0.2	
Tllog3	1166		1163			1169		1163		1170		1195		1158		1170	
liquidus	950		990			966		1000		1018		1018		996		1026	
ugr20/g	298		258			259		253		286		231		256		195	
class	4		3			3		4		4		3		3		3	

Table 1

	17	18	19	20	21	22	23	24
Example								
SiO <sub>2</sub>	68.5	71	68	69	68	67	66	66
Al <sub>2</sub> O <sub>3</sub>	3	0	3	3	3	3	3	4
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	71.5	71	71	72	71	70	69	70
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.3	0.3	0.3	1.3	2.3	3.3	2.5
CaO	7.6	8	8	7.5	7.5	7.5	7.5	7.8
MgO	4.4	4	4	4	4	4	4	3
Na <sub>2</sub> O	15	15.5	15.5	15	15	15	15	15.5
K <sub>2</sub> O	1	1	1	1	1	1	1	1
R <sub>2</sub> O	16	16.5	16.5	16	16	16	16	16.5
SO <sub>3</sub>	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tlog <sub>3</sub>	1165	1142	1154	1170	1164	1157	1150	1155
Liquidus	1006	940	981	974	994	1002	1024	1010
ugR <sub>2</sub> O/g	251	474	251	259	253	236	239	240
Class	3	4	3	3	3	3	3	3

Table 1

Example	25	26	27	28
SiO <sub>2</sub>	66	70	69.5	70.5
Al <sub>2</sub> O <sub>3</sub>	4	2	2	3
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	70	72	71.5	73.5
Fe <sub>2</sub> O <sub>3</sub>	2.5	0.5	0.5	0.3
CaO	6.8	8.5	8.5	8
MgO	4	4	4	4
Na <sub>2</sub> O	15	14.5	14	13
K <sub>2</sub> O	1.5	0.5	1.5	1
R <sub>2</sub> O	16.5	15	15.5	14
SO <sub>3</sub>	0.2	0	0	0.2
Tlog <sub>3</sub>	1164	1166	1165	
liquidus	1014	1006	1005	
ugR <sub>2</sub> O/g	206	261	229	186
Class	3	3	3	3

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## Claims

1. A boric oxide free glass composition capable of being spun into fibres, comprising the following components expressed as weight percent:
 

SiO <sub>2</sub>	66-73
Al <sub>2</sub> O <sub>3</sub>	0.8-5
R <sub>2</sub> O = Na <sub>2</sub> O + K <sub>2</sub> O	14-17.5
CaO	6.5-12
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	69-74
2. A glass composition according to claim 1, further comprising the following components expressed as weight percent:
 

Fe <sub>2</sub> O <sub>3</sub>	0-2
MgO	0-5
SO <sub>3</sub>	0-0.6
3. A glass composition according to claim 1 or 2, wherein the components are present in weight percentages within the following ranges:
 

SiO <sub>2</sub>	67-72.4
Al <sub>2</sub> O <sub>3</sub>	1-4
R <sub>2</sub> O	14.5-17
K <sub>2</sub> O	0.5-2

	Na <sub>2</sub> O	13.5-16.5
	CaO	7-11.2
	Fe <sub>2</sub> O <sub>3</sub>	0.1-2.5
	MgO	0.2-4.4
5	SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	70-73.7

4. A glass composition according to claim 3, wherein the components are present in weight percentages within the following ranges:

	SiO <sub>2</sub>	67-70
10	Al <sub>2</sub> O <sub>3</sub>	2-4
	Na <sub>2</sub> O	14-15.5
	K <sub>2</sub> O	0.5-1.5
	MgO	3-4.5
	CaO	7-8.5
15	Fe <sub>2</sub> O <sub>3</sub>	0.3-2
	SO <sub>3</sub>	0-0.3
	SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	70-72
	Na <sub>2</sub> O + K <sub>2</sub> O	15-16.5

5. An insulating glass fibre production process including the spinning of molten glass at a high temperature in a spinner made from a mechanically alloyed or oxide dispersion strengthened alloy to produce fibres having a composition according to any preceding claim.

6. Insulating glass fibres having a composition according to any one of claims 1 to 4.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4660

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 399 320 (BAYER AG.) * abstract *	1-4,6	C03C13/00 C03C3/087
Y	---	5	
D,X	US-A-4 203 746 (J.A. BATTIGELLI ET AL.) * table IV *	1-4,6	
Y	---	5	
X	CHEMICAL ABSTRACTS, vol. 97, no. 20, 1982, Columbus, Ohio, US; abstract no. 167698Y, M. CZAJA ET AL.: 'Results of the selection of technological and design parameters for production of glass fibers' page 299 ;	1-4,6	
Y	* abstract *	5	
D,Y	US-A-4 402 767 (J.W. HINZE ET AL.) * the whole document *	5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08 SEPTEMBER 1992	Examiner REEDIJK A, M, E.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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